

# BENCH-SCALE STUDY OF SULFUR DIOXIDE REMOVAL BY SODIUM BICARBONATE

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*By*  
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## CERTIFICATE

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Certified that the work presented in this thesis entitled 'Bench-Scale Study of Dry Sulfur Dioxide Removal by Sodium Bicarbonate', by Vijay Prakash has been carried out under my supervision and it has not been submitted elsewhere for a degree.



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## ABSTRACT

In the present work, a bench-scale set-up has been developed for studying the dry sulfur dioxide removal process using solid reactants in a packed bed reactor. Studies on the removal of sulfur dioxide with solid sodium bicarbonate were performed in a sand-bed reactor, to evaluate the performance of sodium bicarbonate for dry sulfur dioxide removal. The test gas ( $\text{SO}_2$  in air) was passed through the sand-bed, containing solid sodium bicarbonate; and the same was monitored at inlet and outlet for sulfur dioxide concentration. Dry sodium bicarbonate showed excellent reactivity with sulfur dioxide and high sorbent utilization was achieved in the bed. The effects of temperature (in the range of,  $150-250^\circ\text{C}$ ) and inlet sulfur dioxide concentration (in the range of 2000-6000 ppm) on the sulfur dioxide removal by sodium bicarbonate has been studied and the results are discussed.

## 1. INTRODUCTION

The man has been deteriorating earth's atmosphere since the days when he flicked fire first in the prehistoric time, and the smoke coming out of the fire was the first anthropogenic pollutant to the earth's atmosphere. Since the atmosphere served as an excellent sink for the disposal of air pollutants, the mankind did not bother much about it.

However, with the development of civilization and human activities, especially urbanization, industrial revolution and explosive growth in thermal power plants, the air pollution has reached an alarming proportion. The problem of air pollution, severely felt in highly industrialized countries, has also begun to raise its head in India. In fact, this concern has provided impetus to mould India's policy on protection of environment and enact series of legislation for prevention and control of pollution. Emission Regulations under Section 17 of the Air (Prevention and Control of Pollution) Act, 1981 have been evolved by Central Board (July, 1984) for selected industries.

Since the implementation of Environmental (Protection) Act, 1986 in India, the thermal power plants and industrial sectors have been facing increasingly stringent air quality emission control requirements.

Sulfur dioxide is one of the five most prevalent anthropogenic air pollutants, the other four being carbon monooxide, particulates, oxides of nitrogen and hydrocarbons. In order to control the sulfur dioxide emission, the removal of sulfur dioxide at source is necessary. Conventional technique of using tall stacks alone may improve air quality locally, but is likely to aggravate the conditions in remote areas. The removal of

sulfur dioxide from the flue gases, before these are discharged in to the atmosphere through the stacks, is commonly referred as flue gas desulfurization (FGD) process.

A great many processes have been proposed for removing sulfur dioxide from flue gases, but relatively few of them have attained the commercial status. The sulfur dioxide content of the flue gas can be reduced by switching to low sulfur fuel or by the processes that remove sulfur from fuel or from the flue gas during or after the combustion processes. At present, the highest level of sulfur dioxide control is achieved by the post combustion processes, namely wet scrubbing and dry scrubbing.

During the middle of 1980's, the dry sulfur dioxide removal processes have emerged as lower cost options to conventional wet scrubbing processes. The dry sulfur dioxide removal processes include spray dryer FGD systems, the injection of dry alkaline sorbent in to the furnace or the post-furnace regions and the use of dry sorbents in a reactor. However, these processes are still under development.

The present work aims at developing a laboratory scale set-up for studying the removal of gaseous sulfur dioxide by solid sorbents dispersed in a sand-bed reactor; while the sulfur dioxide laden test gas passes through it. An experimental study was conducted, using sodium bicarbonate as sorbent; at various temperatures and various sulfur dioxide concentrations.

However, the development of the set-up opens up a wide scope for conducting experimental studies on various sorbents like hydrated lime, sodium carbonate, hydrated magnesia etc. for the purpose of testing, evaluating and comparing the performance of these sorbents.

## 2. LITERATURE REVIEW

The oxides of sulfur are probably the most widespread and most intensely studied of all anthropogenic air pollutants, and the problem of sulfur dioxide removal from the flue gases has been the subject of more research than any other gas purification process (Peavy et.al., 1986 and Kohl et.al., 1979). The present chapter focusses on the occurrence of various oxides of sulfur in the atmosphere, their sources of emission, their effect on environment and present status of sulfur dioxide emission control technologies.

### 2.1 Occurrence of the Oxides of Sulfur in Atmosphere :

#### 2.1.1 Various Species of Oxides of Sulfur in Atmosphere :

The oxides of sulfur present in the atmosphere include six different gaseous compounds - sulfur monooxide ( $SO$ ), sulfur dioxide ( $SO_2$ ), sulfur trioxide ( $SO_3$ ), sulfur tetraoxide ( $SO_4$ ), sulfur sesquioxide ( $S_2O_3$ ) and sulfur heptoxide ( $S_2O_7$ ) (Peavy et.al., 1986).

However, in the study of air pollution control technology, sulfur dioxide and sulfur trioxide are of prime importance, as they constitute more than 99.0 % of total sulfur oxides emission (Stern, 1977).

#### 2.1.2 Sources of Oxides of Sulfur :

The sources of the oxides of sulfur are natural as well as anthropogenic, the latter being of prime importance to an environmental engineer. Among the natural sources of sulfur oxides are volcanic eruptions, forest fires and conversion of hydrogen sulfide in to sulfur dioxide as a result of atmospheric reactions. Burning of fossil fuels, mainly coal, contributes more than 80 % of the total anthropogenic sulfur dioxide emissions, and the fuel

combustion in stationary sources (mainly thermal power plants) and industrial processes are the principal contributors of the sulfur oxides (Peavy et.al., 1986). The automobile exhaust also contributes a little towards anthropogenic sulfur oxide emission but that is of small consequence.

### 2.1.3 Emission of Sulfur Oxides from Various Anthropogenic Sources :

Sulfur is present in significant amounts in coal ( upto about 6 % ) and oil ( upto about 4.5 % ). During the combustion of these fuels, most of the sulfur is oxidized to sulfur dioxide and sulfur trioxide. About 99 % of the total sulfur oxides is emitted as sulfur dioxide and 0.5 to 2 % as sulfur trioxide (Stern, 1977).

Flue gases from combustion processes normally contain less than 0.5 % sulfur dioxide, depending upon the sulfur content of the fuel. Table 1 gives the sulfur dioxide content of combustion gases from several typical fuels (Kohl et.al., 1979).

Table 1  
Sulfur Dioxide Concentrations in Combustion Flue Gases\*  
(Kohl et.al. 1979)

Fuel	SO <sub>2</sub> in Flue Gas (%)
Coal 4 % sulfur	0.35
Fuel oil 2 % sulfur	0.12
Fuel oil 5 % sulfur	0.31
Refinery acid sludge, 40 % sulfuric acid	2.00

\* The values given above are based upon combustion with approximately 15 % excess air.

Sulfur dioxide concentration in stack gas from smelters handling ores containing sulfur may range as high as 8 %. But such

gases are generally favoured for recovery of sulfur values (viz. sulfuric acid, elemental sulfur and liquid sulfur dioxide) rather than gas purification system alone.

## 2.2 Sulfur Dioxide and its Effect on Environment :

Sulfur dioxide is a colourless, nonflammable, nonexplosive gas with a suffocating odour. It has a taste threshold of 0.3 ppm and odour threshold of 0.5 ppm. At a concentration above 3 ppm, it has very pungent irritating odour (Peavy et.al.,1986).

In the atmosphere, the sulfur dioxide is partly converted in to sulfur trioxide, sulfuric acid and sulfate salts, as a result of photochemical and catalytic processes (Calvert,1984). All these pollutants have very detrimental effects on human and animal health, plants, materials and environment. These pollutants tend to irritate the mucous membrane of the respiratory tract and foster the development of chronic respiratory diseases, particularly bronchitis and pulmonary emphysema. Sulfur dioxide when combined with particulate is particularly harmful because the particulate bring the sulfur dioxide or its by-products in to direct prolonged contact with delicate lung tissues (Peavy et.al.,1986).

The injury to plant life by sulfur dioxide is observed in the form of clearly marked dead tissues between the veins or on the margins of the leaves (due to acute exposure), brownish red or bleached white areas on the blades of leaves (due to chronic exposure), reduction in yield of crop etc..The plants are particularly sensitive to sulfur dioxide during intense light, high relative humidity and moderate temperature conditions.

Sulfur compounds' aerosols readily attack building

materials, especially those containing carbonates. The carbonates are replaced by corresponding sulfates, which are, then readily leached away with rains. It can also damage the textiles, paper, leather goods etc.. Excess exposure to sulfur dioxide accelerates the corrosion rate for many metals.

The aerosols of sulfuric acid and other sulfate salts make up 5 to 20 % of the total suspended particulate matter in urban air and they contribute significantly to the reduction of visibility. Another important environmental impact of sulfur dioxide pollution is the formation of acid rains, resulting in to the acidification of water bodies, leaching of nutrients from soil and erosion of carbonaceous rocks etc..

### 2.3 Present Status of Sulfur Dioxide Emission Control Technologies:

Sulfur dioxide is relatively stable in the atmosphere and it remains airborne for a period of approximately 2 to 4 days, during which it may be transported to very long distances. Therefore the problem of sulfur dioxide pollution control is a global one rather than local.

The sulfur appears in the coal in two principal forms - organic sulfur and mineral sulfur. The mineral sulfur appears primarily in the form of pyrites and it occurs as discrete particles, while organic sulfur is an integral part of coal matrix. In fuel oils, the sulfur is present as sulfides, mercaptans, poly-sulfides and thiophenes (Stern,1977). After combustion of these fuels, in power plants, 90 to 95 % of the total sulfur content appears as  $\text{SO}_2$  and 1 to 3 % as  $\text{SO}_3$  in the stack gas. The remainder leaves the furnace in the form of ash (Stern,1977).

The sulfur dioxide content of the stack gas can be reduced by switching to low sulfur fuels or by the processes that remove sulfur from fuels or from flue gases during or after combustion processes (Miller, 1986, Stern, 1977, Muzio et.al., 1987, Offen et.al. 1987 and Kohl et.al., 1979). However, the highest level of sulfur dioxide removal is currently achieved by the post combustion processes, mainly by wet scrubbing and dry scrubbing. Table 2 summarizes the status of individual control technologies, which are currently commercial or nearing commercial operation and have potential retrofit application to existing plants.

#### **2.4 Dry Sulfur Dioxide Emission Control Technologies:**

Though the dry sulfur dioxide emission control technology is not very new, yet it has very less of an operating history than conventional wet scrubbing processes. Most of the dry sulfur dioxide removal processes are still under developmental stage and approaching commercial status slowly (Miller, 1986, Muzio et.al., 1987 and Offen et.al., 1987).

Recently the interest in dry sulfur dioxide removal processes has renewed due to:

(i) the recognition that sorbent performance can be improved by avoiding hot flames,

(ii) successful implementation of various dry sulfur dioxide removal processes in U.S., West Germany etc., and

(iii) the need for a lower cost, moderate sulfur dioxide control technology which may not necessarily require high efficiencies of wet FGD processes.

In a dry sulfur dioxide removal process, the sorbent reacts with sulfur dioxide gas to form a dry product, which is

Table 2

A Summary of Sulfur Dioxide Emission Control Technologies  
(Miller, 1986)

Technology	Commercial Status	Applicability	SO <sub>2</sub> Reduction Potential	Critical Issues
<b>PRECOMBUSTION CONTROL</b>				
*Physical Coal Cleaning	*Commercial	*Most economically applied to coals > 1% S	*10 to 30 % typical *Up to 60 % on easy-to-clean coals	*SO <sub>2</sub> reduction limited by pyrite S content. *Benefits of cleaning need quantification. *Potential heat rate penalty due to increased moisture content and fines loss.
<b>COMBUSTION CONTROL</b>				
*Furnace Dry Sorbent Injection	*Commercial	*Limited applicability	*Depends upon sulfur content of original & alternative coals	*Process not fully characterized. *Potential negative boiler impacts. *Particulate control upgrading required. *Potential adverse impact on ash handling & disposal systems.
*Atmospheric Fluidized Bed Combustion	*Commercial for industrial applications		* >90 % removal	*Fuel feed system *Turndown procedure *Tube erosion and materials longevity *Flyash recycle. *Limestone utilization

Table 2 (continued)

Technology	Commercial Status	Applicability	SO <sub>2</sub> Reduction Potential	Critical Issues
<b>POST COMBUSTION CONTROL</b>				
*Lime and Limestone FGD	*Commercial	*Applicable to virtually all coals.	* >90 % removal achievable	*High capital and operating cost. *Space constraints. *Impact on plant availability.
*Spray Dry FGD	*Commercial	*Applicable to virtually all coals.	* Up to 90 % removal achievable on low sulfur coals.	*Baghouse or ESP improvements may be required. *Process not suitable for gypsum production.
*Dual Alkali FGD	*Commercial	*Not applicable to low sulfur coals (<1% S).	* >90 % removal achievable	*Limestone system difficult to control. *Space constraints
*Recovery of Salable Product FGD	*MGO process commercial	*Applicable to virtually all coals.	* >90 % removal achievable.	*Market for the products must be available. *Processes are relatively complicated and expensive.
*Advanced Throwaway FGD	*Under development	*Applicable over wide range of coals & operating conditions.	* >90 % removal achievable.	*Issues similar to those for lime and limestone FGD.
*Post Furnace Dry Sorbent Injection	*Approaching commercial status	*Potentially applicable to all coals	*70-80 %, on low sulfur coals.	*Sorbent availability & cost. *Spent sorbent disposal problems.

then removed by a downstream particulate collection device. At present, four general approaches are available or under development for bringing the sorbent in to contact with sulfur dioxide (Muzio et.al.1987):

(i) Furnace injection of calcium based compounds.

(ii) Economizer inlet injection of calcium based compounds.

(iii) Post-furnace injection of calcium based compounds in to combustion product at high relative humidity.

(iv) Post-furnace injection of sodium based compounds.

Apart from the above four approaches, sulfur dioxide removal in fixed bed reactors, by regenerable and non-regenerable solid sorbents has also been tried by various researchers (Jorgensen et.al.,1987, Jozewicz et.al.,1988, Gollakota et.al.,1988 and Norman et.al.,1987). The results of the above studies show that the use of fixed bed reactors, especially if coupled with regenerable sorbents, has a good potential for removing sulfur dioxide from flue gases at a very low cost. However, before such a FGD system could be tested in pilot scale plant or under field conditions, a detailed study of the process on a bench scale apparatus is essential.

## 2.5 Summary :

It is apparent from the above discussion that the emission of sulfur dioxide from fossil fuel combustion and other industrial sources represents a serious threat to the environment and severity of sulfur dioxide problem is likely to grow unless remedial measures are taken to reduce its emission to a tolerable limit. Therefore, the control of sulfur dioxide emission at source is necessary. It, however, appears that one will have to rely in

the near future, mainly on FGD processes for controlling sulfur dioxide emission, since the production of sulfur-free fuel will require more development in technology. Furthermore, among the techniques actually available for sulfur dioxide removal from flue gases, dry processes would be advantageous. However, these processes are still under development and they require extensive research in the unexplored area.

### 3. SCOPE OF PRESENT WORK

In spite of high efficiencies of conventional wet scrubbing and spray dryer-based systems for sulfur dioxide emission control, their use is limited by high capital and operating costs and complexity in operation of the system. The dry sulfur dioxide control systems using solid reactants are less complex and are possibly more flexible with respect to operating conditions, like flue gas flow rates and variations in sulfur dioxide concentrations. A number of dry sulfur dioxide removal processes have been developed by several researchers and still being developed (Muzio et.al.,1987 and Offen et.al.,1987 ).The use of solid reactants in a packed bed reactor shows a high potential for sulfur dioxide removal from flue gases (Jorgensen et.al.,1987, Jozewicz et.al.,1987, Gollacota et.al.,1988 and Norman et.al.,1987). However, the usefulness of such a process, in terms of practical applications can be assessed only after detailed studies on the removal of sulfur dioxide by various sorbents in laboratory scale models.

Hence, it is appropriate to develop a laboratory scale set-up for the evaluation of various sorbents for sulfur dioxide removal in packed bed reactors, at various operating conditions. The present investigation was carried out along the following lines :

1. Developing a laboratory scale set-up for the study of sulfur dioxide removal by various solid sorbents, at various operating conditions of temperature, sulfur dioxide concentration, humidity, use of additives with sorbents (which are likely to enhance the removal process ), type and size of bed etc..
2. Evaluating the performance of sodium bicarbonate for

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sulfur dioxide removal from the test gas, in a sand-bed reactor.

Evaluating the effect of inlet sulfur dioxide concentration and temperature on the removal of sulfur dioxide by sodium bicarbonate from the test gas.

## 4. EXPERIMENTAL SET-UP AND TESTING FEATURES

### 4.1 Experimental set-up:

The experimental set-up shown in Figure 1 was developed using the recommendations from other researchers (Ghosh, et.al., 1986, Jorgensen, et.al., 1987 and Jozewicz, et.al., 1988 ).

#### 4.1.1 Test Gas Preparation Systems

In the present work, the test gas was prepared by mixing sulfur dioxide gas and air. The constant flow of air was maintained by an air pump (CompressoVac-70, manufactured by Scientific Instruments Co.Ltd., New Delhi ) and sulfur dioxide was taken from a commercially available sulfur dioxide gas cylinder. The flow of each of the two gases was controlled by a needle valve and then measured with the help of a capillary tube-manometer assembly separately. Then the two gas streams were mixed inside a mixing chamber, which consisted of a vertical glass tube of about 25 mm in diameter and 20 cm long, loosely packed with glasswool. The two gas streams enter the mixing chamber at bottom and after mixing, leave it at the top.

#### 4.1.2 Preheater and Reactor System:

The preheater and reactor system consisted of a reactor fitted above the preheater, so as to minimise the heat losses during the transfer of the test gas from preheater to reactor.

The preheater was used to raise the temperature of the test gas and it consisted of a vertical glass tube of 27 mm internal diameter and 20 cms. long, loosely packed with glass beads and glasswool. The heating coil was wrapped on the outer periphery of the glass tube and it was insulated by putting a

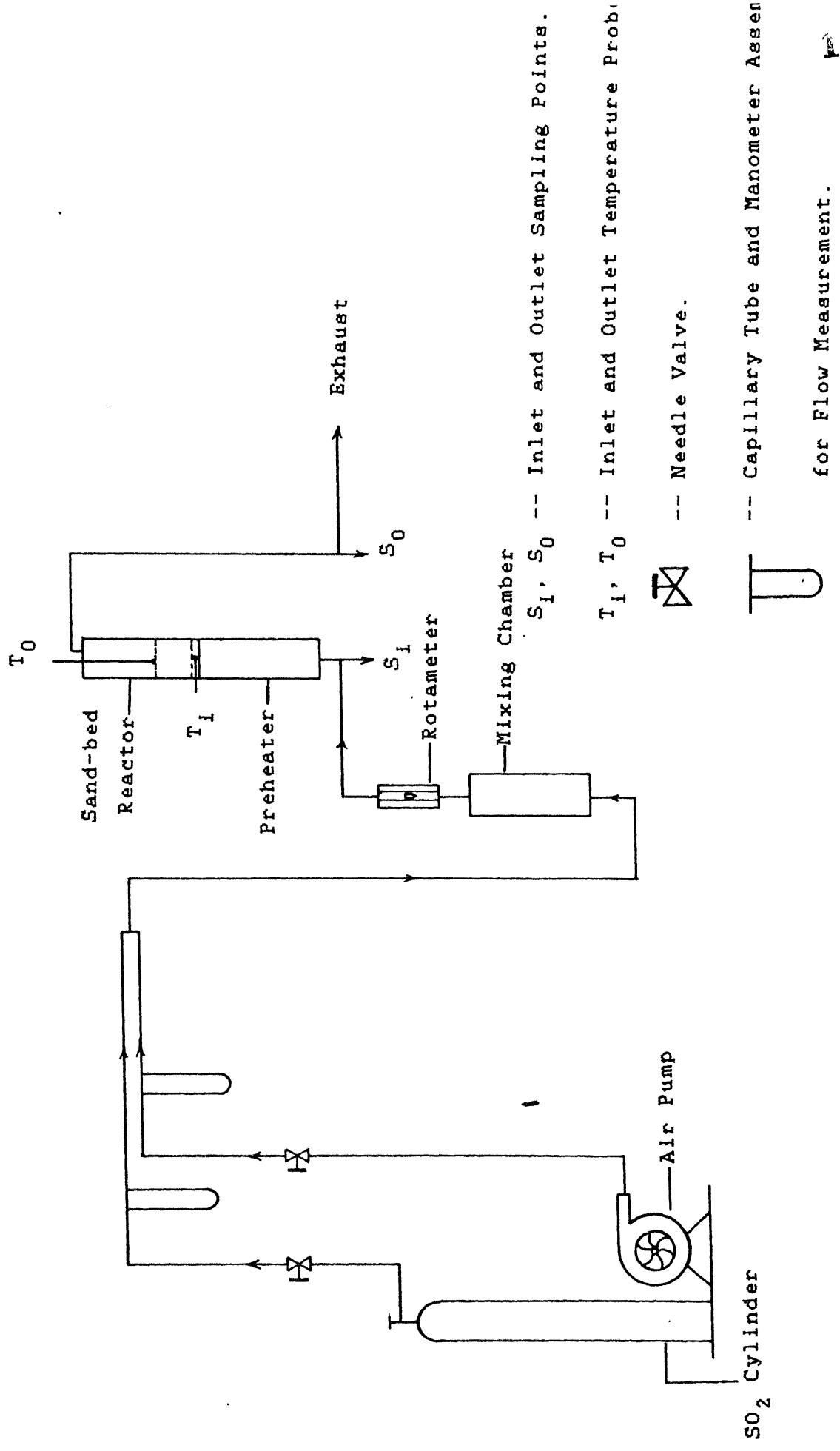


Fig.1 : Experimental Set-up

10 mm thick glasswool jacket. The temperature of the test gas was regulated by heat input by controlling the current through the heating coil.

The sand-bed reactor constitutes the core of the experimental set-up, where the sulfur dioxide in the test gas reacts with the sorbent. It consisted of a vertical glass tube of about 27 mm internal diameter and 20 cm long, containing a fritted glass plate at bottom with some glass wool over it. It has two port holes, one at the top and another at the bottom of the sand-bed, for the measurement of temperature at these points. A chromel alumel thermocouple with a galvanometer was used for the measurement of temperature. The reactor has provisions for varying the height of the sand-bed from 6 cms to 10 cms.

#### **4.1.3 Sampling Points:**

The sulfur dioxide concentration of the test gas was measured at two points - at the inlet of the preheater and reactor system, and at the outlet of the reactor. These sampling points are shown in Fig.1, as  $S_i$  and  $S_o$  respectively. The gas was sampled with the help of an impinger and aspirator bottle arrangement. The effluent gas was allowed to cool down to the room temperature, before it was sampled.

#### **4.2 Testing Features:**

A detailed description of the operating conditions and testing features of the present study is given in Table 3.

Table 3

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## Testing Features

## 1. Sand-Bed

Type of Sand	Local Sand
Geometric Mean Size	450 micron
Bulk Density	1.464 gm./ cm. <sup>3</sup>
Porosity	44 percent
Amount of Sodium Bicarbonate	
in the Bed	1 gm./40 gm. of Sand
Diameter of Bed	27 mm.
Height of Bed	60 mm.

## 2. Operating Conditions

Composition of Test Gas	SO <sub>2</sub> in Air
Concentration of SO <sub>2</sub> in	
Test Gas	2000-6000 ppm
Moisture Content of	
Test Gas	150-175 ppm
Temperature of Test Gas	
at inlet of reactor	150 - 250° C
Flow Rate of Test Gas	2 litres/min.
Space Velocity of Test Gas	0.98 second <sup>-1</sup>
Residence Time of Test Gas	
in Sand-Bed	1.025 seconds

## 5. MATERIALS AND METHODS

### 5.1 Materials :

#### 5.1.1 Glassware :

All the glassware used in the present study was of 'Pyrex' quality, manufactured by Borosil Glass Works Ltd., Bombay and marketed under the brand name 'Corning'.

#### 5.1.2 Water :

Water used in the preparation of the reagents and all other experimental work was laboratory distilled water.

#### 5.1.3 Chemicals :

All the chemicals used for preparation of reagents, for estimation of sulfur dioxide concentration were of analytical reagent grade.

#### 5.1.4 Sorbent Bed :

For the preparation of sorbent bed, local sand passing through 500 micron sieve and retained on 425 micron sieve (thereby giving geometric mean size of 450 micron) was used. The sand was first washed with tap water and finally with distilled water, so as to remove any adhering impurity. Then, it was dried at 103°C for 24 hrs..

As suggested by other researchers (Jorgensen et.al., 1987, Jozewicz et.al., 1988 and Karlsson et.al, 1983), one gram of sodium bicarbonate was dispersed per 40 gram of sand for making the sorbent bed. The sodium bicarbonate used in the bed was of analytical reagent grade. A stock solution of sodium bicarbonate (50 gram per litre) was prepared. To prepare a sorbent bed, 50 gram of clean dry sand was taken in a clean dry petridish, and 25

ml of stock sodium bicarbonate solution was transferred in to it. Now, the contents of petridish were mixed well and the petridish was kept in an oven at 103°C for 24 hrs. for drying. After transferring the sorbent from the petridish to the reactor, the petridish was weighed. The increase in the weight of the petridish due to sodium bicarbonate adhering on it was deducted from the actual quantity of sodium bicarbonate added to the sand. This gave the exact amount of sodium bicarbonate present in the sorbent bed.

#### 5.1.5 Test Gas :

The test gas used in all experiments consisted of sulfur dioxide gas from commercially available sulfur dioxide gas cylinder, with air as dilutant. The desired concentration level of the sulfur dioxide in the gas mixture was maintained by individual and accurate control of flows of air and sulfur dioxide gas. The two gas streams were mixed in a mixing chamber to ensure the uniform composition of the gas mixture. The moisture content of the test gas, as determined by relative humidity calculations, was of the order of 150 to 175 ppm.

### 5.2 Experimental Methodology :

#### 5.2.1 Analytical Technique Used for Sulfur Dioxide

##### Estimation:

The concentration of sulfur dioxide in the gas mixture was measured by 'Sodium Tetrachloromercurate Method', as given in IS:5182 (Part II)-1969. In this method, sulfur dioxide is absorbed in an absorbing solution (sodium tetrachloromercurate solution, 0.1 M), where it forms stable dichlorosulfonitomercurate. The amount of sulfur dioxide absorbed, is then estimated by the colour

produced, when acid-bleached p-rosaniline hydrochloride and formaldehyde solutions are added to it. The absorbance of the solution, at 560 nm was measured with the help of Spectrophotometer 106 (Systronics Pvt. Ltd., New Delhi) and it was matched with the standard plot to get amount of sulfur dioxide present in absorbing solution. From this value of sulfur dioxide present in absorbing solution, the concentration of sulfur dioxide in the gas mixture was calculated by the method given in the Appendix A.

A standard plot for sulfur dioxide estimation is shown in Fig. 2. For higher concentrations of sulfur dioxide in the gas mixtures sampled, suitable dilutions were made before the analysis.

#### 5.2.2 Experimental Technique :

In the present study, a series of experiments were performed to test the reactivity of sodium bicarbonate with sulfur dioxide gas. The process variables expected to influence the sulfur dioxide capture by sodium bicarbonate, were identified as the sulfur dioxide concentration in the gas mixture, the temperature of the gas stream at the inlet of the reactor and the relative humidity. However, the effect of first two variables only, namely sulfur dioxide concentration of the gas mixture and the temperature of the gas could be included in the present study.

Prior to the testing, the concentration of sulfur dioxide in the gas mixture and the temperature at the inlet of the reactor were ensured to be fairly constant. Then, the gas mixture was passed through the reactor containing sorbent bed and the same was sampled at inlet and outlet sampling points, at different time

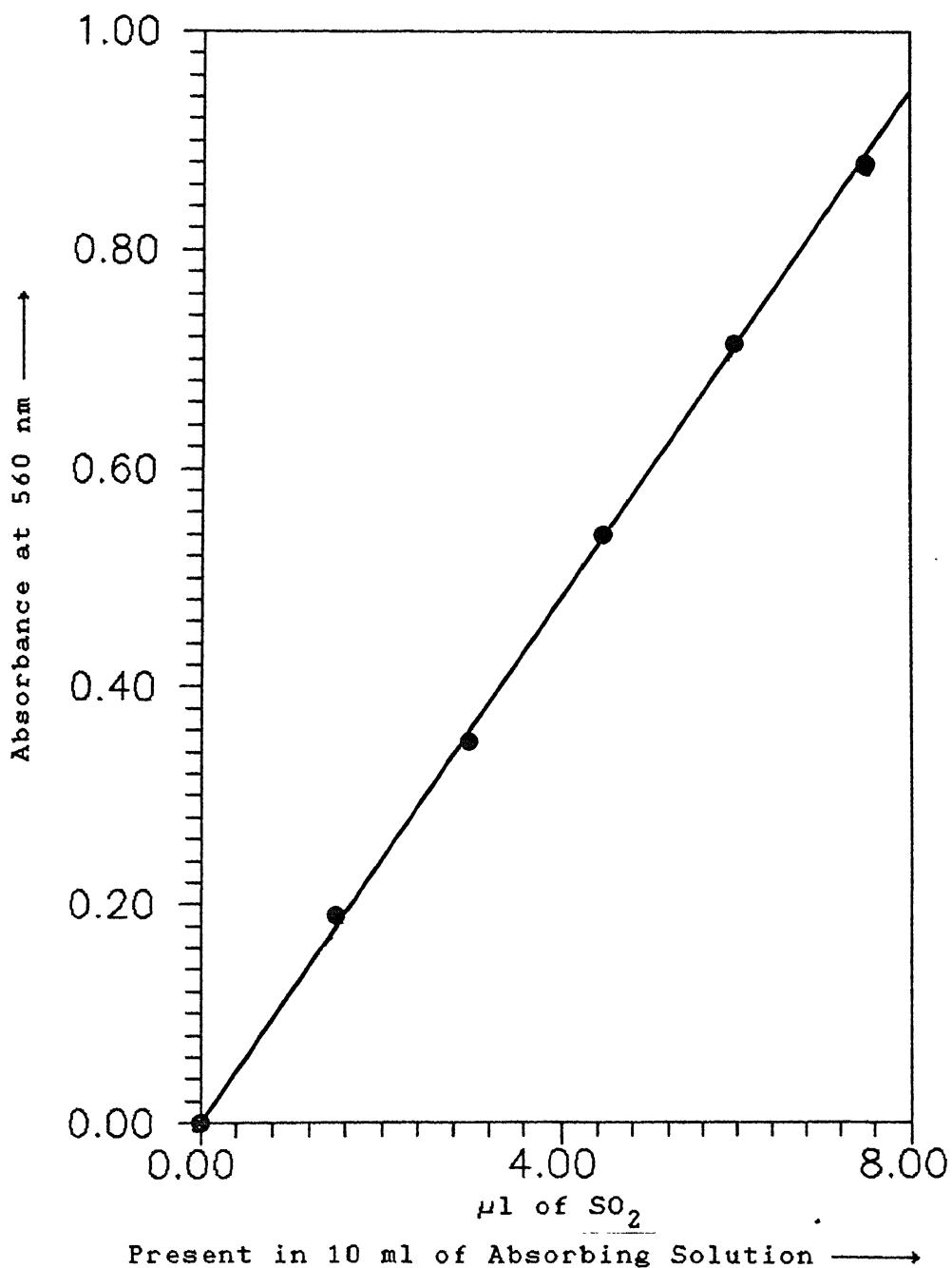


Fig.2 : Standard Plot for Estimation of  $\text{SO}_2$  by Sodium Tetrachloromercurate Method.

intervals. For each sampling, 50 ml of the gas sample was passed through 25 ml of absorbing solution with the help of an impinger and aspirator bottle arrangement. The samples were collected and analyzed by aforesaid Sodium Tetrachloromarcurate Method.

## 6. RESULTS AND DISCUSSION

### 6.1 Results:

#### 6.1.1 Breakthrough Curves from Packed Bed Experiments:

Table 4 shows the experimental data for sulfur dioxide breakthrough curves under different operating conditions of temperature and inlet sulfur dioxide concentration. A typical breakthrough curve for sulfur dioxide absorption in a sand bed reactor is shown in Fig. 3. Initially, the sulfur dioxide concentration at the exit of the sand-bed was not detectable. However, the same increased gradually with the progress of exposure time and approached that of the influent gas, indicating that no further absorption of sulfur dioxide was taking place in the reactor. The total amount of sulfur dioxide absorbed during each experimental run was found by integrating the area above the observed breakthrough curve. The ratio of total sulfur dioxide absorbed ( in moles ), to the amount of sodium bicarbonate present in the bed ( in moles ) was calculated for each experimental run and this parameter, termed as 'conversion', was used to compare the sulfur dioxide absorption achieved in the bed at different operating conditions.

#### 6.1.2 Effect of Temperature on Sulfur Dioxide Removal:

Table 5 shows the dimensionless exit concentrations ( $C/C_0$ ), the ratio of effluent sulfur dioxide concentration to the inlet sulfur dioxide concentration ) versus exposure time, calculated from the breakthrough curves as obtained above. Fig. 4 shows the  $C/C_0$  versus time curves for various experiments conducted at different temperatures, the sulfur dioxide concentration in the test gas being the same. The sulfur dioxide absorption achieved in the packed bed reactor, expressed as conversion ( mol.  $\text{SO}_2$  / mol.  $\text{NaHCO}_3$  ), and the

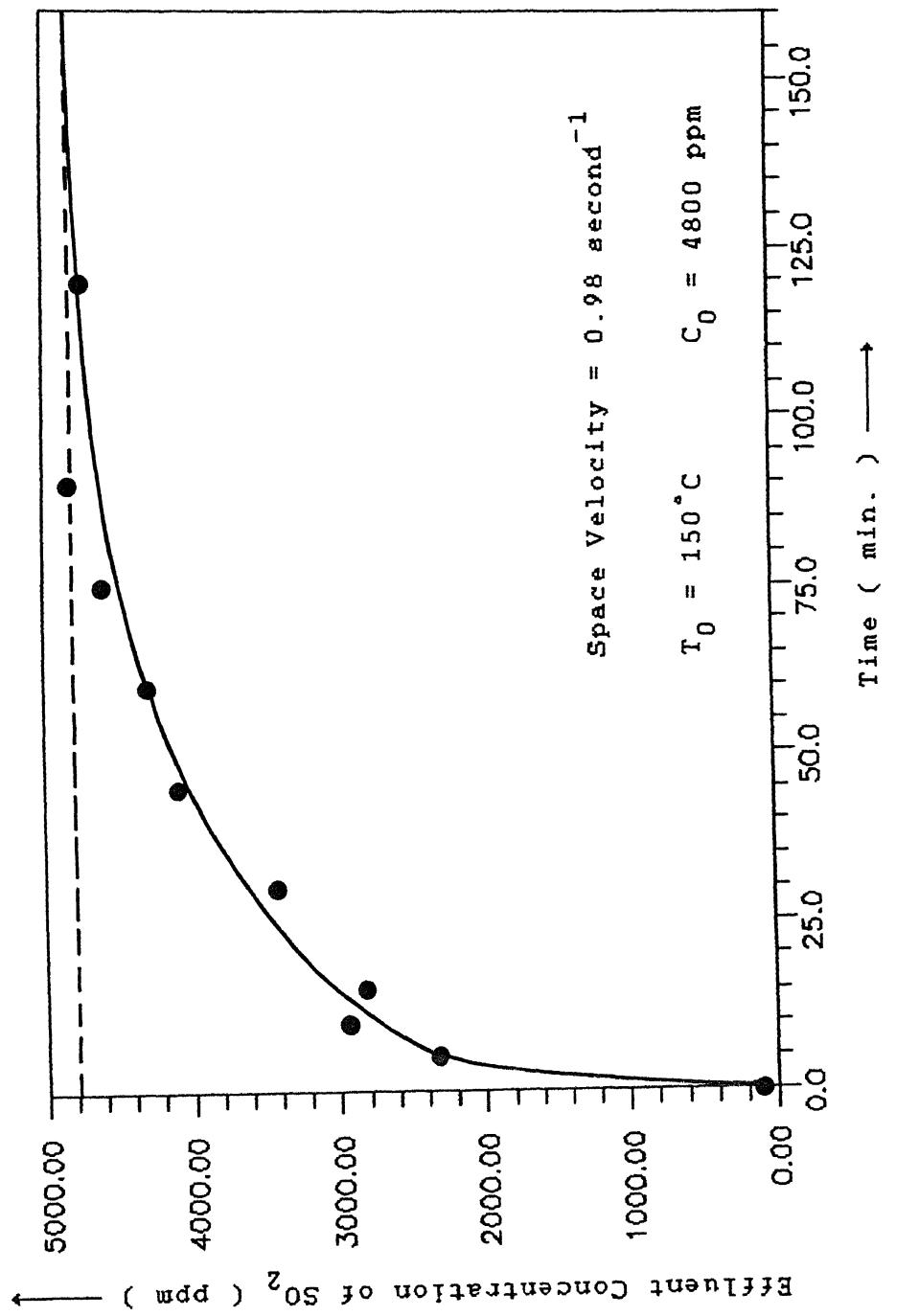


Fig. 3 : A Typical Breakthrough Curve for Absorption of  $\text{SO}_2$  by  $\text{NaHCO}_3$  in a Sand-bed Reactor.

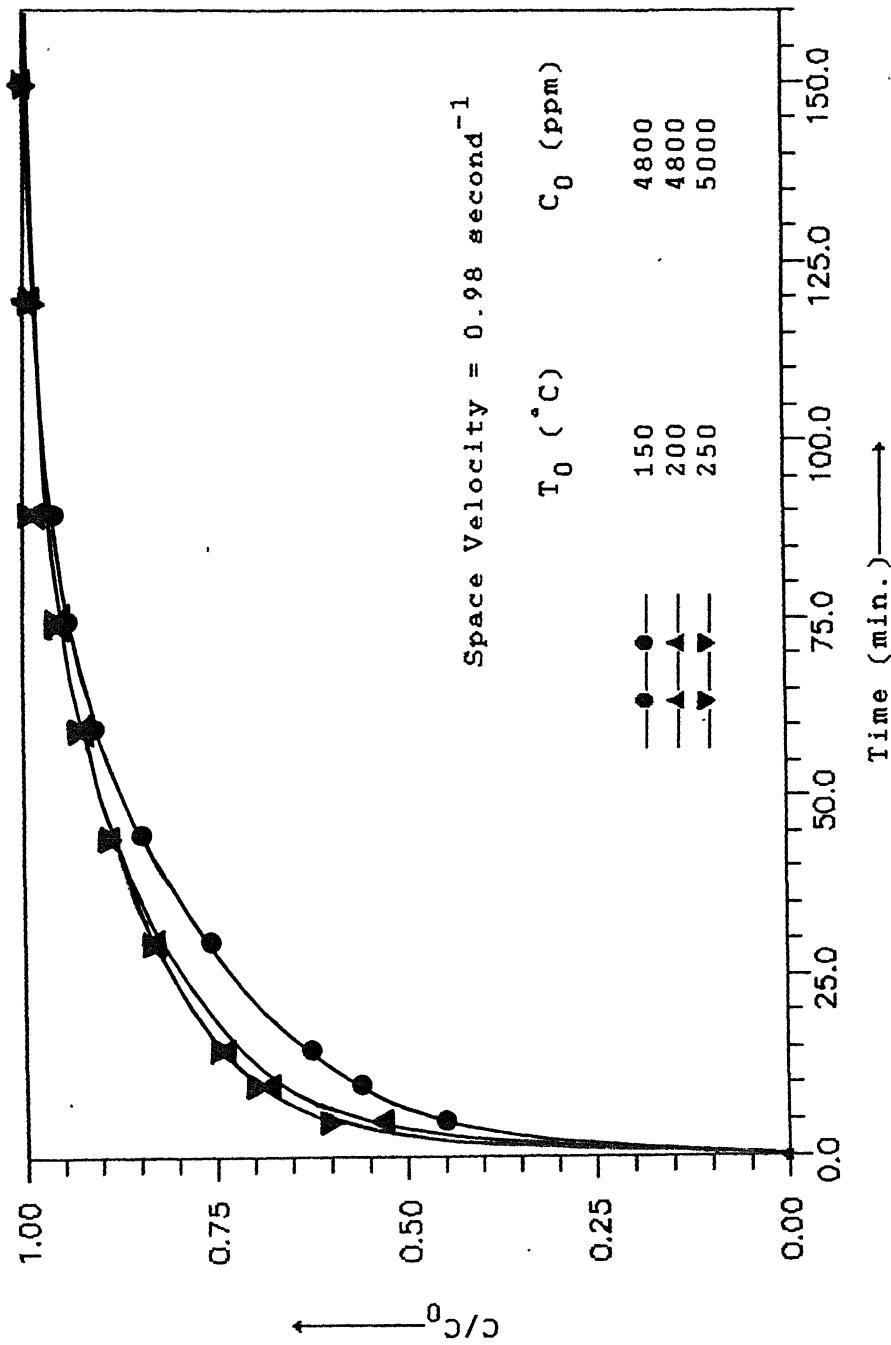


Fig. 4 : Effect of Temperature on Sulfur Dioxide Breakthrough Curves

Table 4

Experimental Data of Breakthrough Curves for Sulfur Dioxide Removal by Sodium Bicarbonate

Time (min.)	Concentration of $\text{SO}_2$ at Outlet					
	$C_0 = 2000 \text{ ppm}$ $T_0 = 150^\circ\text{C}$	$C_0 = 4000 \text{ ppm}$ $T_0 = 150^\circ\text{C}$	$C_0 = 4800 \text{ ppm}$ $T_0 = 150^\circ\text{C}$	$C_0 = 6000 \text{ ppm}$ $T_0 = 150^\circ\text{C}$	$C_0 = 5000 \text{ ppm}$ $T_0 = 250^\circ\text{C}$	$C_0 = 4800 \text{ ppm}$ $T_0 = 200^\circ\text{C}$
1	64	60	108	183	27	31
5	89	20	2325	2443	2818	2974
10	40	77	2940	3686	3505	3307
15	1053	2372	2814	3578	4650	3560
30	1567	3075	3412	4265	4002	3560
45	1752	3750	4086	5108	4718	4650
60	1736	3540	4280	5350	4735	4002
75	1837	3740	4592	5740	4971	4297
90	1938	3720	4820	6028	5173	4381
120	2056	4010	4736	5919	5097	4684

Table 5

Calculated Values of  $C/C_0$  from Idealized Breakthrough Curves

at Different Times

Time (min.)	C/C <sub>0</sub> Values					
	C <sub>0</sub> =4800 ppm T <sub>0</sub> =150 °C	C <sub>0</sub> =4800 ppm T <sub>0</sub> =200 °C	C <sub>0</sub> =5000 ppm T <sub>0</sub> =250 °C	C <sub>0</sub> =2000 ppm T <sub>0</sub> =150 °C	C <sub>0</sub> =4000 ppm T <sub>0</sub> =150 °C	C <sub>0</sub> =6000 ppm T <sub>0</sub> =150 °C
1	0.00	0.00	0.00	0.00	0.00	0.00
5	0.45	0.53	0.604	0.02	0.00	0.4
10	0.56	0.68	0.698	0.05	0.044	0.53
15	0.625	0.735	0.745	0.3	0.525	0.66
30	0.755	0.83	0.829	0.78	0.756	0.742
45	0.844	0.885	0.885	0.87	0.838	0.85
60	0.906	0.917	0.93	0.92	0.89	0.92
75	0.953	0.942	0.955	0.95	0.925	0.97
90	0.974	0.958	0.99	0.97	0.995	1.00
120	1.00	0.99	1.00	0.99	0.99	1.00
150	1.00	1.00	1.00	1.00	1.00	1.00

percent utilization of sodium bicarbonate achieved in the bed, for various experiments, are given in Table 6.

The  $C/C_0$  versus time curves indicate that, with increase in the temperature of the test gas, the initial breakthrough of sulfur dioxide occurs quicker but the rate of exhaustion of the bed is slower. However, the total sulfur dioxide removal achieved in the bed and percent utilization of sodium bicarbonate is almost same.

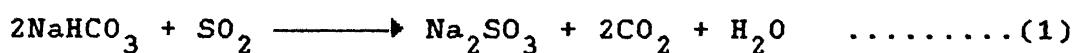
#### 6.1.3 Effect of Inlet Sulfur Dioxide Concentration on Sulfur Dioxide Removal:

Fig. 5 shows the  $C/C_0$  versus time curves for various experiments conducted at different sulfur dioxide concentrations, the temperature of the test gas being the same. Data for the same has been reported in Table 5. The sulfur dioxide absorption achieved in the reactor and percent utilization of sodium bicarbonate achieved in the bed, for various experiments are given in Table 7.

The  $C/C_0$  versus time curves indicate that, with increase in the inlet sulfur dioxide concentration, the initial breakthrough of sulfur dioxide occurs quicker. However, as indicated by Table 7, the percent utilization of sodium bicarbonate increases with higher inlet concentrations of sulfur dioxide.

#### 6.2 Discussion:

The above behaviour of sodium bicarbonate for absorption of sulfur dioxide can be explained on the basis of the chemical reactions involved in the process:



However, at the temperatures higher than the calcination temperature of  $\text{NaHCO}_3$  (temp.  $> 135^\circ \text{C}$ ), the calcination of  $\text{NaHCO}_3$  also starts inside the reactor and the removal of  $\text{SO}_2$  proceeds

Table 6

**Effect of Temperature on Percent Utilization of Sodium Bicarbonate in Sand - Bed**

Concentration of Sulfur Dioxide at Inlet,  $C_0 = 4800$  ppm

$T_0$ (°C)	Conversion (mol. $SO_2$ / mol. $NaHCO_3$ )	Percent Utilization of $NaHCO_3$
150	0.446	89.2
200	0.404	80.8
250	0.441	88.2

Table 7

**Effect of Inlet Sulfur Dioxide Concentration on Percent Utilization of Sodium Bicarbonate in Sand - Bed**

Temperature of Test Gas at Inlet =  $150^\circ C$

$C_0$ (ppm)	Conversion (mol. $SO_2$ / mol. $NaHCO_3$ )	Percent Utilization of $NaHCO_3$
2000	0.284	56.8
4000	0.303	60.6
4800	0.446	89.2
6000	0.499	99.8

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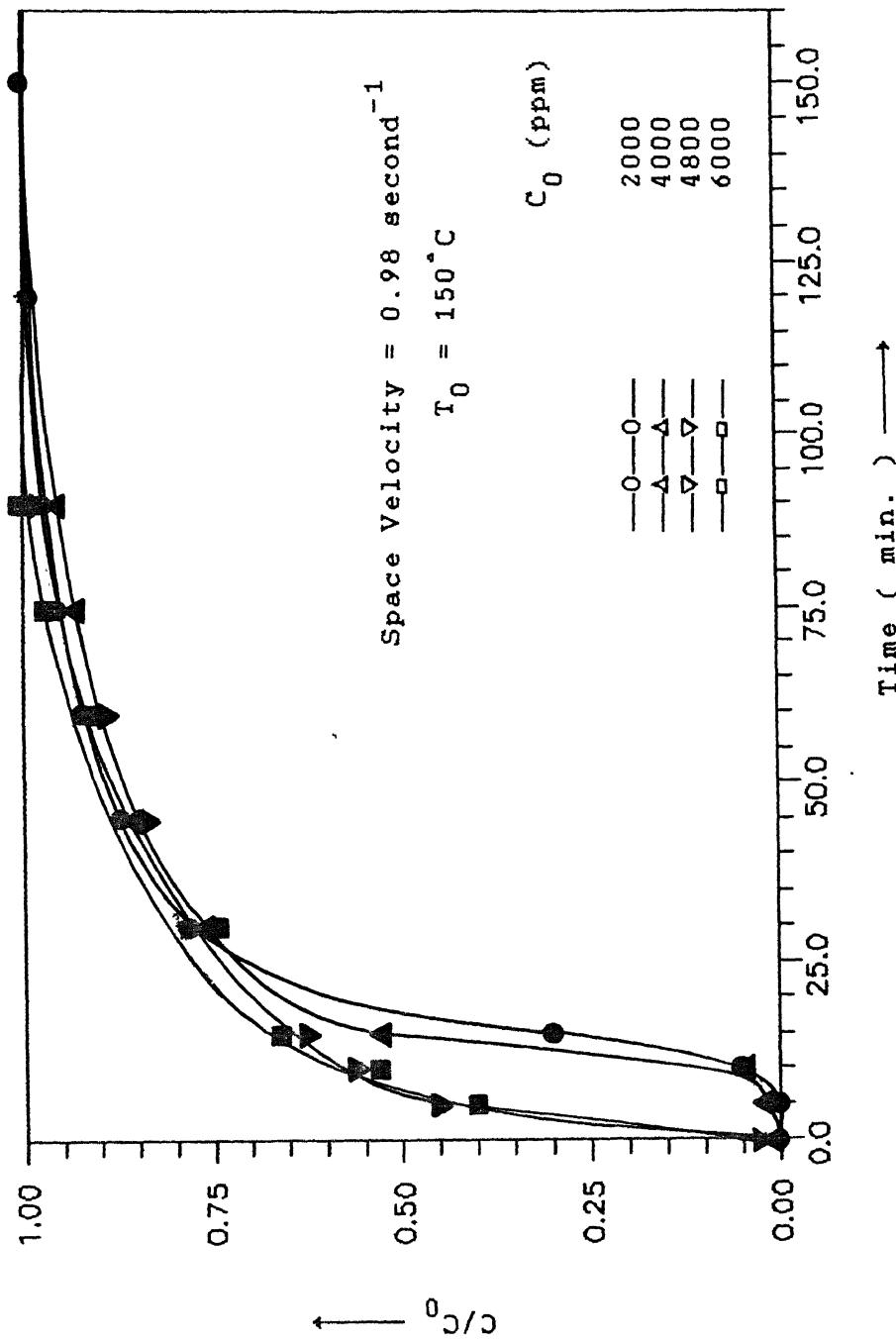
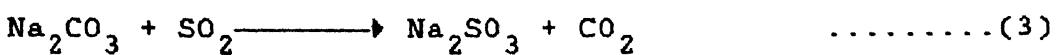
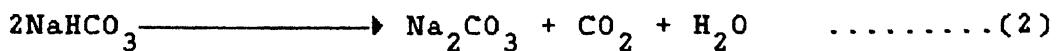


Fig. 5 : Effect of Inlet  $\text{SO}_2$  Concentration on Sulfur Dioxide Breakthrough Curves

according to the following reactions:



Later, the  $\text{Na}_2\text{SO}_3$  formed in the reactions given above is converted to  $\text{Na}_2\text{SO}_4$ , as indicated below:



It may be mentioned that the calculated values of free energy change ( Appendix B ), using the standard heats of formation and molal entropy values from literature (Weast, 1986 ) indicate that these reactions are feasible. Furthermore, the above reactions indicate that sodium bicarbonate loses three moles of gaseous end products (namely  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) per mole of sulfur dioxide absorbed, resulting into the increase in porosity of the sodium bicarbonate particle. Therefore the reaction of sulfur dioxide with sodium bicarbonate is not likely to be susceptible to blinding.

With increase of temperature above  $135^{\circ}\text{C}$ , the calcination of sodium bicarbonate starts and the gaseous end products of calcination, diffusing out of the sodium bicarbonate particles may hinder the penetration and diffusion of sulfur dioxide into the sodium bicarbonate particles, thereby reducing the reaction rate. That is perhaps the reason for quicker initial breakthrough of sulfur dioxide observed at higher temperatures. However, the carbon dioxide and water molecules diffusing out of the sodium bicarbonate particle increases the porosity of the particle, which ultimately results into better utilization of sodium bicarbonate. Further, since the number of carbon dioxide and water molecules released per mole of sodium bicarbonate is same, irrespective of whether it was calcined first, or reacted straightaway, the total

utilization of sodium bicarbonate achieved in all the cases was almost same irrespective of the temperature of the test gas.

In the present study, the sand-beds consisted of the identical quantities of sand (of same geometric mean size ) and sodium bicarbonate. Therefore, at higher concentrations of  $\text{SO}_2$  in test gas, the quicker initial breakthrough of sulfur dioxide is expected. However, with the increase in the concentration of sulfur dioxide in the test gas, the driving force behind the diffusion of sulfur dioxide through the product layer ,on the surface of sodium bicarbonate particle, also increases ; resulting into higher sorbent utilization.

## 7. SUMMARY AND CONCLUSIONS

In the present work, a laboratory scale set-up has been developed as a useful tool for studying the dry sorbent reaction with gaseous sulfur dioxide, in a packed bed reactor. The set-up can be used for further studies on dry sulfur dioxide removal by different solid sorbents and additives ( which are reported in literature to enhance the sulfur dioxide capture by the sorbents), in the packed bed reactors at different process conditions.

The present study on sulfur dioxide removal by sodium bicarbonate, in a sand-bed reactor, indicates that the porosity of sodium bicarbonate particles increases with the progress of the reaction of sulfur dioxide with it; and that the reaction is not susceptible to blinding. This also suggests that high sorbent utilization can be achieved in a sodium compound based dry sulfur dioxide removal system. Furthermore, the sulfur dioxide absorption achieved in this process, is less sensitive to the variations in temperature ( in the temperature range studied, 150-250°C ), as compared to the variations in sulfur dioxide concentration of the test gas at inlet. However, since the study did not include the kinetic studies on the reaction of sulfur dioxide with sodium bicarbonate, the concrete elucidation of the system performance could not be made.

## 8. SUGGESTIONS FOR FUTURE WORK

The present study and the study by others show the potential usefulness of the packed bed reactors for dry sulfur dioxide removal processes. Such a system, if developed with regenerable sorbent, may prove to be an economical and viable technique for sulfur dioxide emission control at smaller sources, which may not afford conventional sulfur dioxide scrubbing systems. However, before such a process can be utilized under pilot scale testing and field testing, it would be essential to conduct a detailed study on the reaction of sulfur dioxide with the sorbent, in a laboratory scale set-up.

Magnesium oxide, which shows excellent reactivity with sulfur dioxide ( Egan et.al., 1986 ), can be used as a regenerable sorbent for sulfur dioxide removal. The end product of the reaction, which contains mainly magnesium sulphite, can be easily regenerated to magnesium oxide and sulfur dioxide rich gas stream. The study on magnesium oxide process for sulfur dioxide removal, in a packed bed reactor may be carried out along the following lines:

(i) To study the reaction kinetics of the reaction in a differential reactor and to measure the initial rate of reaction in an integral reactor.

(ii) To study the effect of various process variables on sulfur dioxide capture by magnesium oxide; i.e. the concentration of sulfur dioxide in the test gas, the temperature of the test gas, relative humidity of the test gas, space velocity of the test gas passing through the reactor etc..

(iii) To study the effect of addition of various deliquescent salt additives ( like  $\text{CaCl}_2$ ,  $\text{Na}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2$  etc. ), on sulfur dioxide removal, which are reported in literature to enhance the sulfur dioxide removal.

(iv) To study the various methods of dispersion and conditioning of the sorbent on different types of packing materials like sand, activated alumina etc..

(v) To test the regenerability of the sorbent bed and degree of inactivation of the sorbent (conversion to non-regenerable form ) achieved after each run.

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## APPENDICES

### A : Calculation of $\text{SO}_2$ Concentration in Gas Sample from Absorbance Data :

Let A = Absorbance at 560 nm.

$V_1$  =  $\mu\text{l}$  of  $\text{SO}_2$  present in 10 ml of absorbing solution corresponding to absorbance A (from Std. Plot).

$V_2$  = Volume of absorbing solution taken in impinger for gas sampling.

n = The dilution number.

$V_3$  = Volume of gas sample.

$$\begin{aligned}\text{Concentration of } \text{SO}_2 \text{ (ppm)} &= \frac{V_1}{10} \times V_2 \times n \times \frac{1000}{V_3} \\ &= 100 \times n \times \frac{V_1 \times V_2}{V_3}\end{aligned}$$

In the present work, 50 ml of gas was sampled in 25 ml of absorbing solution in each sampling. Therefore,

$$\text{Concentration of } \text{SO}_2 \text{ in gas sample (ppm)} = 50 \times n \times V_1$$

The concentration of  $\text{SO}_2$  obtained by above method was within  $\pm 5\%$  of the calculated values obtained from the flows of  $\text{SO}_2$  and air through the capillary tube-manometer assembly.

**B : Thermodynamic Calculations for the Sulfation Reactions:**

The values of the standard enthalpies and entropies of various compounds involved in the reaction are summarised below (Weast, 1986):

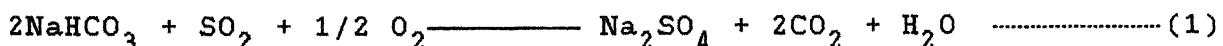
Compound	$\Delta H_{298}^{\circ}$ (kcal./mol.)	$\Delta S_{298}^{\circ}$ (cal./mol. $^{\circ}$ K)
$\text{NaHCO}_3$ (c)	-227.25	24.30
$\text{Na}_2\text{CO}_3$ (c)	-270.24	32.26
$\text{Na}_2\text{SO}_3$ (c)	-263.1	34.88
$\text{Na}_2\text{SO}_4$ (c)	-331.52	35.75
$\text{SO}_2$ (g)	-70.944	59.30
$\text{CO}_2$ (g)	-94.051	51.06
$\text{H}_2\text{O}$ (g)	-57.796	45.105
$\text{O}_2$ (g)	0	49.003

From the values given above,  $\Delta H_{298}^{\circ}$  (the net change in enthalpy) and  $\Delta S_{298}^{\circ}$  (the net change in entropy) values were calculated for each of the reactions. To test the feasibility of the reaction, at the temperatures of the test gas,  $\Delta G$  values (the net change in free energy of the reaction) were calculated by the following equations:

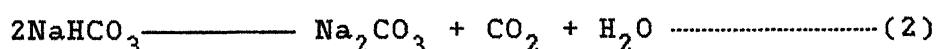
$$\Delta G = \Delta H_{298}^{\circ} - T \cdot \Delta S_{298}^{\circ}$$

..... where T=Temperature ( $^{\circ}$ K)

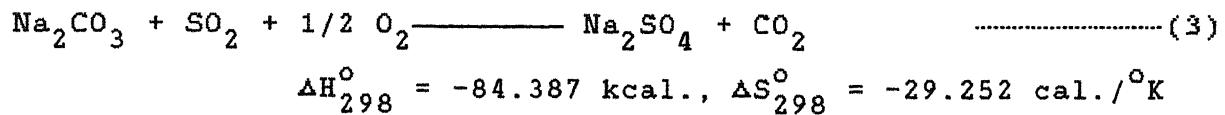
The calculation of  $\Delta G$  values is summarised below:



$$\Delta H_{298}^{\circ} = -51.974 \text{ kcal.}, \Delta S_{298}^{\circ} = 50.57 \text{ cal./}^{\circ}\text{K}$$



$$\Delta H_{298}^{\circ} = 32.413 \text{ kcal.}, \Delta S_{298}^{\circ} = 79.723 \text{ cal./}^{\circ}\text{K}$$



Reaction No.	$\Delta G_{150}^{\circ}\text{C}$ (kcal.)	$\Delta G_{200}^{\circ}\text{C}$ (kcal.)	$\Delta G_{250}^{\circ}\text{C}$ (kcal.)
1.	-73.37	-75.90	-78.43
2.	-1.32	-5.31	-9.29
3.	-72.01	-70.55	-69.08